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Glenn A. Fugate*[a]; Kenji Takeshita[a]; Tatsuro Matsumura[b]
[a] Chemical Resource Laboratory, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama, Japan [b] Japan Atomic Energy Agency, 2-4 Shirane, Shirakata, Tokai-mura, Naka-gun, Ibaraki, Japan

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Separation of Americium (III) and Lanthanide (III) Ions using TPEN Analogs

Glenn A. Fugate,[1]* Kenji Takeshita,[1] and Tatsuro Matsumura[2]
[1]Chemical Resource Laboratory, Tokyo Institute of Technology,
Nagatsuta, Midori-ku, Yokohama, Japan
[2]Japan Atomic Energy Agency, 2-4 Shirane, Shirakata, Tokai-mura,
Naka-gun, Ibaraki, Japan

Abstract: N,N,N′,N′-tetrakis(2-pyridylmethyl)-1,2-ethylenediamine (TPEN) has been shown previously to exhibit a high separation factor for the separation of americium (III) and europium (III). Application of TPEN is limited due to the solubility of the material under acidic conditions ($pH < 4$). A variety of analogs were synthesized in this study to examine effects caused by various structural modifications in an effort to retain the selectivity of the parent compound while decreasing solubility in acidic media. Results indicate that the substitution at the ethylene linker of TPEN eliminates the ability of the compound to separate americium (III) over europium (III).

Keywords: Americium; Europium; Soft donor; TPEN

INTRODUCTION

One of the issues being addressed to develop and improve the nuclear fuel cycle is the ability to separate trivalent minor actinide ions from waste which may contain large quantities of lanthanide ions. This separation may play an important role to reduce the volume and heat load of the radioactive waste which must be sequestered in a repository. Waste reduction may be accomplished using a combination of new process

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Address Correspondence to Kenji Takeshita, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan. E-mail: takeshit@res.titech.ac.jp

technologies, new waste storage forms and/or the development of technologies to transmute long lived isotopes with all of the processing requiring improved separation capability for minor actinide separation from lanthanide materials.

The separation of trivalent actinide and lanthanide ions can be difficult as these ions have similar charge and ionic radii. Past work has shown that the f-element ions can be separated based upon the slightly softer Pearson acidity of the actinide series using compounds which contain soft donor groups, such as N,N,N′,N′-tetrakis(2-pyridylmethyl)-1, 2-ethylenediamine (TPEN).

TPEN (Fig. 1) has shown the ability to effectively separate trivalent minor actinide ions from trivalent lanthanide ions under mildly acidic conditions (pH 4-6) (1–4) and can also be used in the separation of a variety of d-block metals (5–8) which are common and potentially commercially useful fission products in nuclear waste. Solvent extraction studies have reported TPEN to be as much as 20 to 200 times more selective for americium (III) compared to europium (III) (1,9), depending on extraction conditions, but its application is limited by the solubility of this compound in acidic aqueous media ($pH < 4$). The purpose of this study is to synthesize a variety of TPEN analogs that attempt to decrease the aqueous solubility of the compound while maintaining the selectivity of this extractant for minor actinide ions.

Several studies have examined effects such as varying the length of the alkyl linker chain between the aliphatic amine groups (10,11), functionalization of the ethylene linker group (9,10), functionalization of the pyridine rings (12), and replacement of the pyridine rings with other nitrogen containing rings such as pyrazine (11). Comparisons between these studies

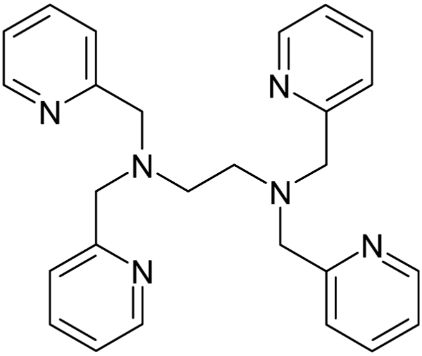


Figure 1. Structure of N,N,N′,N′-tetrakis(2-pyridylmethyl)-1,2-ethylenediamine (TPEN).

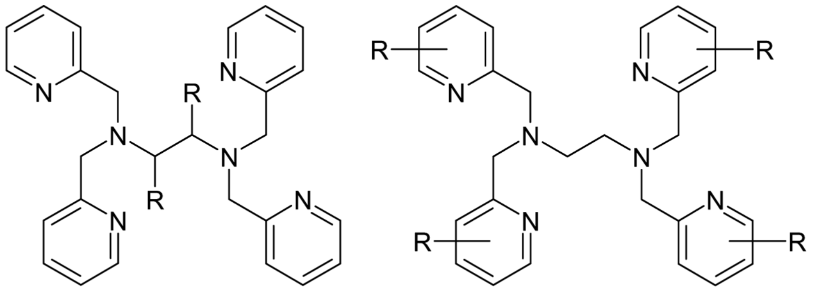


Figure 2. Potential sites (R) for modification of TPEN.

sometimes can be difficult as the extraction behavior of TPEN varies, depending upon the organic phase, pH, and aqueous media.

This study has focused on the synthesis and characterization of different classes of TPEN compounds. TPEN can be modified at two practical sites, shown in Fig. 2, which includes the ethylene linker group and the pyridyl group. Substitution at the methyl group of the pendant arm were not pursued as they would likely result in increased steric restriction of the coordination site, slower coordination kinetics, and reduced thermodynamic stability. This study focuses on coordination chemistry effects caused replacing the ethylene linker group with aromatic compounds and examines the potential application of bis substituted TPEN analogs for the separation of americium (III) and europium (III) ions.

EXPERIMENTAL

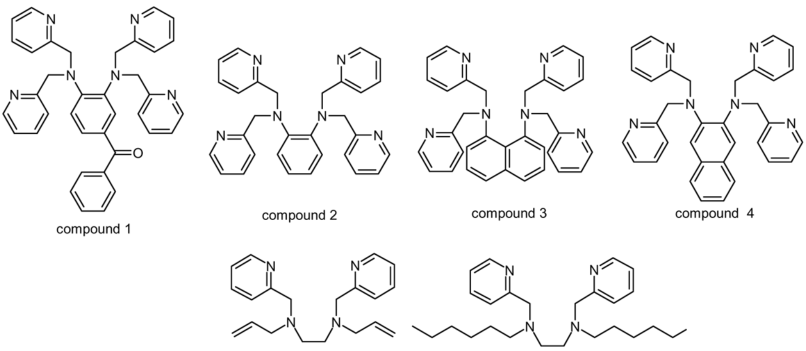
Materials

All reagents were obtained from commercial suppliers in the highest grade which could be commercially obtained and used without further purification. All aqueous solutions were made with deionized water.

Synthesis

Synthesis of N,N,N′,N′-tetrakis(2-methylpyridyl)-3,4-diaminobenzophenone (1)

Compound 1 (Fig. 3) was synthesized was synthesized based upon a procedure from the literature (13). 3,4-Diaminobenzene (0.486 g, 2.29 mmole) and 2-chloromethylpyridine hydrogen chloride (1.59 g, 9.72 mmole) were combined in 12.5 mL of 5.1 M sodium hydroxide. A catalytic amount of hexadecyltrimethylammonium chloride was added



compound 1

compound 2

compound 3

compound 4

compound 7

compound 8

Figure 3. Structures of compounds synthesized in this study that were used in solvent extraction experiments which include N,N,N′,N′-tetrakis(2-methylpyridyl)-3,4-diaminobenzophenone (compound 1), N,N,N′,N′-tetrakis(2-methylpyridyl)-1,2-phenylenediamine (compound 2), N,N,N′,N′-tetrakis(2-methylpyridyl)-1,8-napthalenediamine (compound 3), N,N,N′,N′-tetrakis(2-methylpyridyl)-2,3-napthalenediamine (compound 4), N,N′-bis(2-meythylpyridyl)-N,N’-bisallyl-1,2-ethylenediamine (compound 7), and N,N′-bis(2-meythylpyridyl)-N,N′-bishexyl-1,2-ethylenediamine (compound 8).

as a phase-transfer catalyst. The solution was stirred vigorously for 1 week at 20 ± 1°C. The product was extracted into chloroform and the solvent was removed under reduced pressure at 40°C. The compound was purified on an alumina gel column using a gradient elution which went from 1:1 chloroform:hexane to chloroform. The solvent was removed under reduced pressure at 40°C to yield a dark brown oil. Yield: 0.196 g, 14.8%. MS: M^+ 576.0 (576.7).

Synthesis of N,N,N′,N′-tetrakis(2-methylpyridyl)-1,2-phenylenediamine (2)

Compound 2 (Fig. 3) was synthesized was synthesized in a similar manner as compound one, combining 1,2-phenylenediamine (1.11 g, 6.12 mmole), 2-chloromethylpyridine hydrogen chloride (1.97 g, 12.0 mmole) and a catalytic amount of hexadecyltrimethylammonium chloride in 20 mL of 5.1 M sodium hydroxide. The solution was stirred vigorously for 2 days at 20 ± 1°C. 2-Bromomethylpyridine hydrogen bromide (3.18 g, 12.6 mmole) was added in several small additions over the reaction time to provide a move reactive reagent to force formation of the sterically hindered tetrakis compound. The product was extracted into chloroform and the solvent was removed under reduced pressure at 40°C. The compound was purified by elution with chloroform from an alumina gel column to yield a yellow oil after removing the solvent under reduced pressure at 40°C. Yield: 0.495 g (17.1%). MS: tetrakis-Na^+ 495.0 (495.6). Elemental Analysis for $C_{30}H_{28}N_6$: C, 76.24; H, 5.97; N, 17.78. Found: C, 71.77; H, 6.08; N, 18.07.

Synthesis of N,N,N′,N′-tetrakis(2-methylpyridyl)-1, 8-napthalenediamine (3)

Compound 3 (Fig. 3) was synthesized in a manner similar to compound 1, combining 1,8-naphthalenediamine (0.583 g, 3.68 g) with stoichiometric amounts of the other reagents in 15 mL of acetonitrile. The solution was refluxed for 5 hours at 80°C and the stirred vigorously for 2 days at 20 ± 1°C. The solvent was removed under reduced pressure at 50°C. The compound was purified using an alumina column and a gradient elution beginning with dichloromethane and ending with chloroform. The solvent was removed under reduced pressure at 30°C to produce a solid. The product was then extracted into diethyl ether for an additional purification. The solvent was removed under reduced pressure at 20°C to produce an orange oil. Yield: 0.398 g, 20.6%. MS: M^+ 522.8 (522.7). Elemental Analysis for $C_{34}H_{30}N_6$: C, 78.13; H, 5.79; N, 16.08. Found: C, 55.45; H, 4.86; N, 10.99.

Synthesis of N,N,N′,N′-tetrakis(2-methylpyridyl)-2, 3-napthalenediamine (4)

Compound 4 (Fig. 3) was synthesized was synthesized in the same manner of compound 1 by combining 2,3-naphthalenedimaine with stoichiometric amounts of the other reagents. Potassium carbonate (2.41 g, 17.4 mmole) was used as a less reactive basic reagent and the reaction was performed in 10 mL of acetonitrile. The system was stirred vigorously for 4 days at 50°C. The solvent was removed under reduced pressure at 40°C. The resulting oil was extracted into diethyl ether and then the organic phase was dried with magnesium sulfate, filtered, and evaporated under reduced pressure at 40°C to yield a brownish-orange oil. Yield: 0.374 g, 54.1%. MS: tetrakis-Na^+ 545.1 (545.7). Mass spectrometry results indicated that the product had a small amount of bis and tris impurities. Elemental Analysis for $C_{34}H_{30}N_6$: C, 78.13; H, 5.79; N, 16.08. Found: C, 32.56; H, 5.42; N, 12.49.

Synthesis of N,N′-bis(2-methylpyridyl)-1,2-ethylenediimine (5)

Compound 5 (Fig. 3) was synthesized based on a similar reaction found in the literature (15) by combining 1,2-ethylenediamine (0.900 g, 15.0 mmole) and 2-pyrdiylcarbaldehyde (3.41 g, 31.8 mmole) in 20 mL of methanol. The solution was in contact with 4 Å molecular sieves. The reaction was refluxed at 70°C for 17 hours, resulting in a change in the color of the solution from yellow to orange-yellow. The solution was filtered and evaporated under reduced pressure at 20°C, producing an orange oil. The product was recrystallized in warm hexane to form pale yellow needle crystals. Yield: 2.18 g, 61.0%. MS: M^+ 238.9 (238.3).

Synthesis of N,N′-bis(2-methylpyridyl)-1,2-ethylenediamine (6)

Compound 6 was synthesized by dissolving compound 5 (1.97 g, 8.26 mmole) into 10 mL of methanol which had been dried over 4 Å molecular sieves. Sodium borohydrate (0.863 g, 22.8 mmole) was dissolved into 13 mL of methanol. Both solutions were chilled in an ice bath. The sodium borohydrate solution was added dropwise over 5 minutes to the solution of compound 5 with vigorous stirring. The solution was stirred vigorously for 40 minutes in an ice bath before being heated to reflux for 15 minutes. The solution was allowed to cool and stirred at 20 ± 1°C for 15 hours before being evaporated under reduced pressure at 20°C, producing a yellow liquid. The product was dissolved into water and the product was extracted into dichloromethane. The organic phase was removed under reduced pressure at 20°C, yielding a pale yellow liquid. Yield: 1.517 g, 75.8%. MS: 243.2 (242.3), $M\text{-}Na^+$ 265.0 (265.3).

Synthesis of N, N′-bis(2-methylpyridyl)-N,N′-bisallyl-1, 2-ethylenediamine (7)

Compound 7 (Fig. 3) was synthesized by combining compound 6 (0.330 g, 1.38 mmole), 3-allyl bromide (0.513 g, 4.24 mmole), and a catalytic amount of hexdecyltrimethylammonium chloride in 10 mL of 1.31 M potassium carbonate. The solution was stirred vigorously for 3 days at 20 ± 1°C and was noted to have formed a two phase system. The product was extracted into diethyl ether and the solvent was removed under reduced pressure at 20°C to yield a yellow oil. Heating was avoided to minimize potential reactions of the allyl group. Yield: 0.225 g, 50.6%. MS: $M\text{-}Na^+$ 345.0 (345.5).

Synthesis of N,N′-bis(2-methylpyridyl)-N,N′-bishexyl-1, 2-ethylenediamine (8)

Compound 8 (Fig. 3) was synthesized in a similar manner as compound 7 using 1-hexyl bromide bromide (1.39 g, 8.41 mmole) to compound 6 (0.44 g, 1.84 mmole). Compound 8 was purified using alumina, rinsing impurities off the column with dichloromethane followed by elution of the product using chloroform. The solvent was removed under reduced pressure at 30°C to yield a yellow oil. Yield: 0.547 g, 73.1%. MS: M-H$^+$ 411.2 (410.6), M-Na$^+$ 433.1 (433.6).

Solvent Extraction

Aliquots of known activity of ^{241}Am and ^{152}Eu was added to the 1.0 M ammonium nitrate aqueous phase and the pH was adjusted to the desired range. The organic phase consisted of 1.0 mM solution of the ligand in nitrobenzene. The extraction was performed by contacting 3 mL volumes of the aqueous and organic phases for 90 minutes with agitation at 25.0 ± 0.1°C. The final equilibrium pH was determined for each sample after shaking. The distribution ratio, D_M, was determined for americium (III) and europium (III) as the ratio of the concentration of the metal ion in the organic and aqueous phases. The concentrations of ^{241}Am and ^{152}Eu were determined by gamma spectroscopy (59.54 keV peak of ^{241}Am and 121.78 keV peak of ^{152}Eu) using a high purity germanium spectrometer. The separation factor, $SF_{Am/Eu}$, was calculated as the ratio of the distribution ratios of americium (III) and europium (III) ions.

RESULTS AND DISCUSSION

Results from elemental analysis reported for compounds 2, 3, and 4 showed significantly lower values for C, H, and N than expected. These measurements were made several months after the synthesis of the compounds and likely reflect decomposition of the materials. Other work performed in the Takeshita group has observed that the neutral species is prone to decomposition. The elemental analyses of other compounds in the work were not performed as similar low results were expected.

The results from the solvent extraction studies are listed in Table 1. All hexadentate compounds showed decreased selectivity when compared to TPEN under similar extraction conditions. The separation factor and distribution ratios reported for the cis and trans cyclohexane TPEN analogs (N,N,N′,N′-tetrakis(2-methylpyridyl)-1,2-diaminocyclohexane) in 1-octanol (9) are similar to the values reported for aromatic TPEN analogs in this study (compounds 1, 2, and 4), suggesting that the acidity of the amine is not a significant factor in the selectivity of TPEN. Molecular calculations of several of the structures of interest were performed using a simple energy minimization algorithm (MM2, Chem3D Pro, v. 11.0.1). These calculations indicate that there is a change in the bite size for TPEN type systems, depending upon what linker group is present.

Table 1. Solvent extraction results

Compound	pH	Am D (org/aq)	Eu D (org/aq)	$SF_{Am/Eu}$
TPEN[9]*	4.16	2.0×10^{0}	9.9×10^{-3}	45
	5.15	1.5×10^{1}	3.3×10^{-1}	200
1	2.10	$<10^{-4}$	$<10^{-4}$	–
	3.06	$<10^{-4}$	$<10^{-4}$	–
	4.01	$<10^{-4}$	$<10^{-4}$	–
	4.85	6.01×10^{-3}	3.17×10^{-3}	1.9
	5.89	7.66×10^{-2}	4.75×10^{-2}	1.6
2	2.25	$<10^{-4}$	$<10^{-4}$	–
	3.14	$<10^{-4}$	$<10^{-4}$	–
	4.06	$<10^{-4}$	$<10^{-4}$	–
	4.99	3.50×10^{-3}	2.26×10^{-3}	1.6
	5.98	3.73×10^{-3}	1.59×10^{-3}	2.3
3	2.20	$<10^{-4}$	$<10^{-4}$	–
	3.09	$<10^{-4}$	$<10^{-4}$	–
	4.06	4.42×10^{-4}	4.66×10^{-4}	0.9
	4.91	2.82×10^{-3}	7.94×10^{-4}	3.6
	5.96	7.78×10^{-3}	1.26×10^{-3}	6.2
4	3.04	$<10^{-4}$	$<10^{-4}$	–
	4.01	$<10^{-4}$	$<10^{-4}$	–
	4.83	$<10^{-4}$	9.43×10^{-4}	–
	5.86	3.83×10^{-3}	2.04×10^{-3}	1.9
7	3.05	$<10^{-4}$	1.14×10^{-4}	–
	4.06	$<10^{-4}$	$<10^{-4}$	–
	4.97	$<10^{-4}$	6.80×10^{-4}	–
	5.71	3.25×10^{-3}	7.25×10^{-4}	4.5
8	3.06	$<10^{-4}$	$<10^{-4}$	–
	4.04	$<10^{-4}$	$<10^{-4}$	–
	4.89	$<10^{-4}$	1.10×10^{-3}	–
	5.76	1.27×10^{-3}	7.40×10^{-4}	1.7

*Extraction conditions: 0.1 M ammonium nitrate, nitrobenzene, 1.0 mM TPEN, 30 minutes contact time.

The amine bite gap of the lanthanum complex of an ethylene system (TPEN) was calculated as 2.70 ± 0.01 Å which shows good agreement with the value of 2.73 Å which can be calculated from the crystal structure (14). Similar analyses were performed for aromatic systems (compounds 1, 2, and 4), *trans*-cyclohexane, and *cis*-cyclohexane with the calculated amine bite size being 3.03 ± 0.01 Å, 2.85 ± 0.01 Å, and 2.91 ± 0.01 Å, respectively. The changes in the amine bite size show a small increase but there is a significant decrease the selectivity of the compounds for extracting trivalent minor actinide ion extraction from lanthanide ions.

The amine bite size of the propylene linked TPEN analog can be calculated to be 3.10 ± 0.01 Å. The propylene system has been shown to have similar distribution values for americium (III) but does not have the selectivity found in TPEN. This is because the distribution ratio of europium (III) is approximately 2 orders of magnitude higher for the propylene analog versus the ethylene compound (11). These large changes in selectivity with small to moderate changes in the amine bite size suggest that the steric hindrance and structure of the ligand in the complex is more likely the case in the change in selectivity instead of the bite size or the acidity of the amine groups.

Although americium (III) is only extracted at the highest pH of the study, compounds 7 and 8 appear to have similar distribution ratios as most of the other hexadentate compounds examined in this study. This may be a result of improved interactions between metal ions and the aliphatic amines which are less sterically hindered in the tetradentate compounds. The acidity of these amine sites would be expected to be significantly different from each other and from the hexadentate compounds, further suggesting that the aliphatic amine acidity is not related to the ability of the compounds to selectively extract the minor actinide species and that the increased structural reorganization required by the TPEN analogs is the cause of the decrease in the extraction selectivity.

CONCLUSIONS

Karmazin et al. suggest that the lack selectivity for the compounds of this study suggests that the selectivity exhibited by TPEN lies in its ability to organize the complexes ligand structure in a manner that reduces bond length and bond angle strain within its own structure in the complex. This is supported by results from this work which indicate that structural strain introduced by an aromatic linker in a TPEN analog decrease the selectivity of the compound for trivalent minor actinide ions. The decrease in distribution ratio observed for both europium (III) and americium (III) extractions indicates that ring structures decrease the stability of the complexes which is likely a result of increased steric effects in the structure. Future work on TPEN type extraction compounds must focus on functionalization of the pyridine ring to improve solubility and acid range issues which occur in TPEN.

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